Open metal sites(OMSs) and Lewis basic sites(LBSs) -functionalized copper-organic framework with high CO_2 uptake performance and highly selective CO_2/N_2 and CO_2/CH_4 separation

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Table S1. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**[a]

1			
Cu1-N1#1	1.98(5)	Cu1-N2	2.003(9)
Cu1-O5	2.11(7)	Cu2-O2	1.945(15)
Cu2-O4#2	1.974(16)	Cu2-O6	2.20(6)
N1#1-Cu1-N1#3	80(5)	N1#1-Cu1-N2#4	160.6(15)
N1#3-Cu1-N2#4	95(2)	N2-Cu1- N2#4	83.5(16)
N1#1-Cu1-O5	97.4(18)	N1#3-Cu1-O5	97(2)
N2-Cu1-O5	101.9(17)	O2-Cu2-O2#5	86.2(13)
O2-Cu2-O4#6	88.7(9)	O2-Cu2-O4#7	167.4(7)
O4#6-Cu2-O4#7	93.9(13)	O2-Cu2-O6	99.5(11)
O4#6-Cu2-O6	92.7(10)		

[a] Symmetry transformations used to generate equivalent atoms: #1 x, -y+1/2, z+1/2; #2 -x+1/2, -y+1, z-1/2; #3 -x+1, -y+1/2, z+1/2; #4 -x+1, y, z; #5 x, -y+1, z; #6 -x+1/2, y, z-1/2, #7 -x+1/2, -y+1, z-1/2.

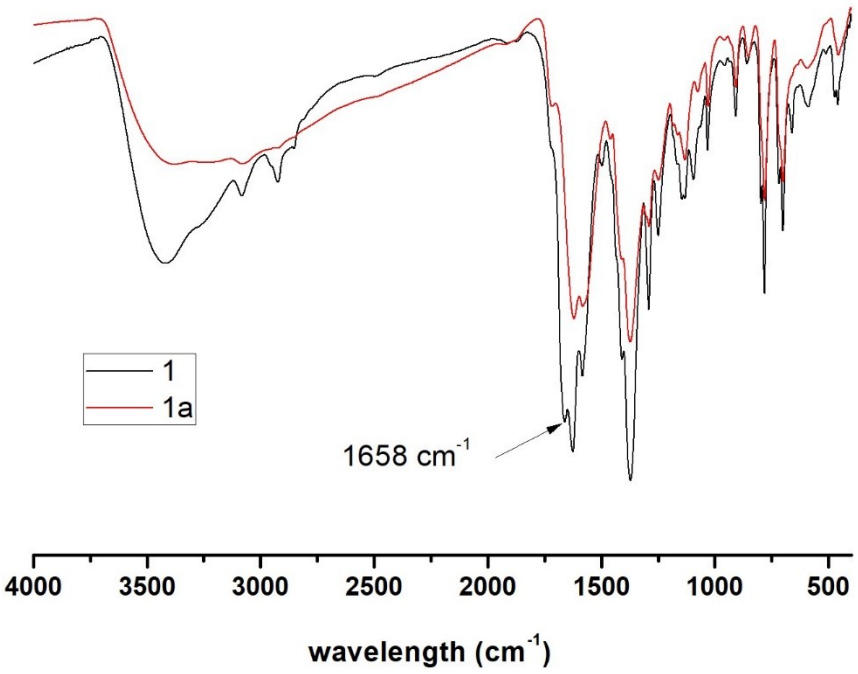
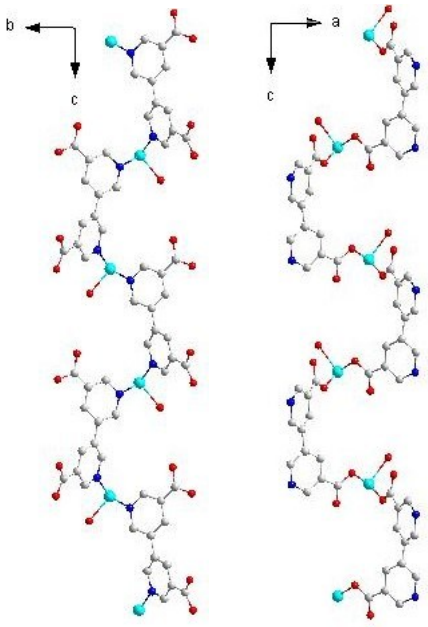


Fig. S1 The FT-IR spectra of **1** and **1a**. The characteristic C=O vibration at 1658 cm^{-1} of DMA in **1** is absent in **1a**, indicating the complete removal of DMA.



(a) (b)

Fig. S2 The zigzag 1D chains along c-axis, with Cu1-Cu1 distance of 7.736 Å for (a) and Cu2-Cu2 distance of 7.770 Å for (b).

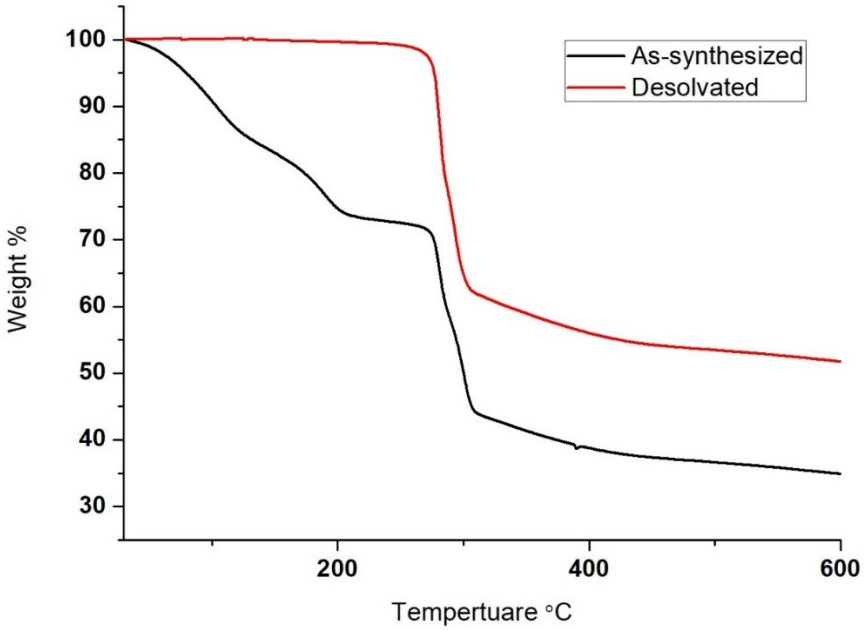


Fig. S3 TGA curves

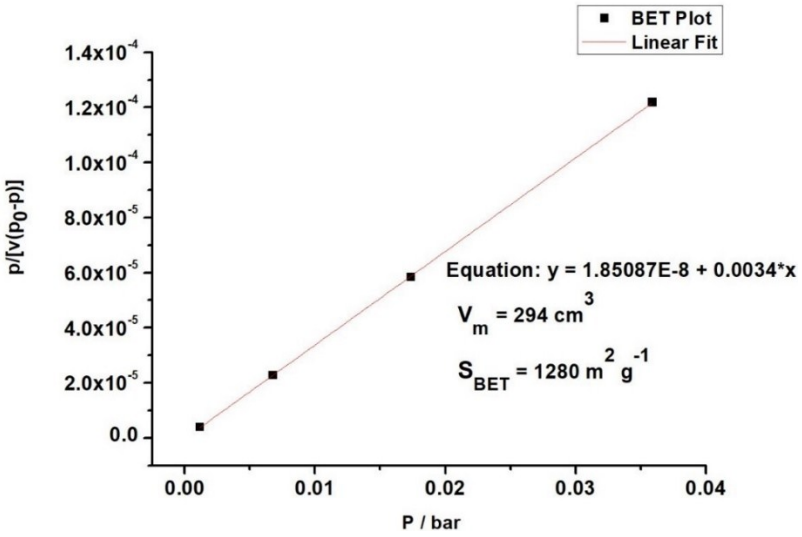


Fig. S4 The BET plot calculated from N_2 isotherm of **1a**

Table S2 Comparison of the best CO_2 adsorption performances of MOFs. Note: the highest values of each parameter were highlighted in boldface.

MOF (common name)	D_C (g cm^{-3})	CO_2 uptake at 298 K and 1 bar		Ref
		(mmol g^{-1})	(mmol cm^{-3})	

Mg-MOF-74	0.920	**8.6**	7.912	S1
MAF-X27ox	1.354	6.70	9.07	S2
MAF-X25ox	1.227	7.14	8.76	S2
FJI-H14	1.167	7.63	8.91	S3
$[Cu_2(BPDC)_2]$	1.147	**8.6**	**9.86**	**This work**
Co_2(dobdc)	1.177	6.96[#1]	8.20[#1]	S4
Ni_2(dobdc)	1.194	5.8[#1]	6.93[#1]	S4
SIFSIX-2-Cu-i	1.246	5.41	6.74	S5
MAF-66	1.128	5.0	5.6	S6
HKUST-1	0.879	4.86	4.27	S7
bio-MOF-11	1.234	5.0	6.17	S8

dobdc = 4,4'-dioxido-3,3'biphenyldicarboxylate; SIFSIX= SiF_6^{2-} anions. [#1] 296 K.

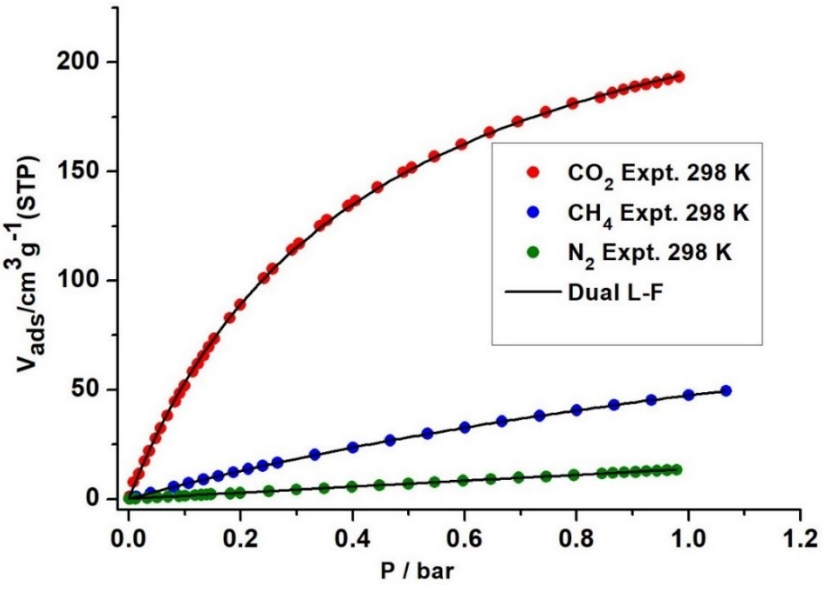
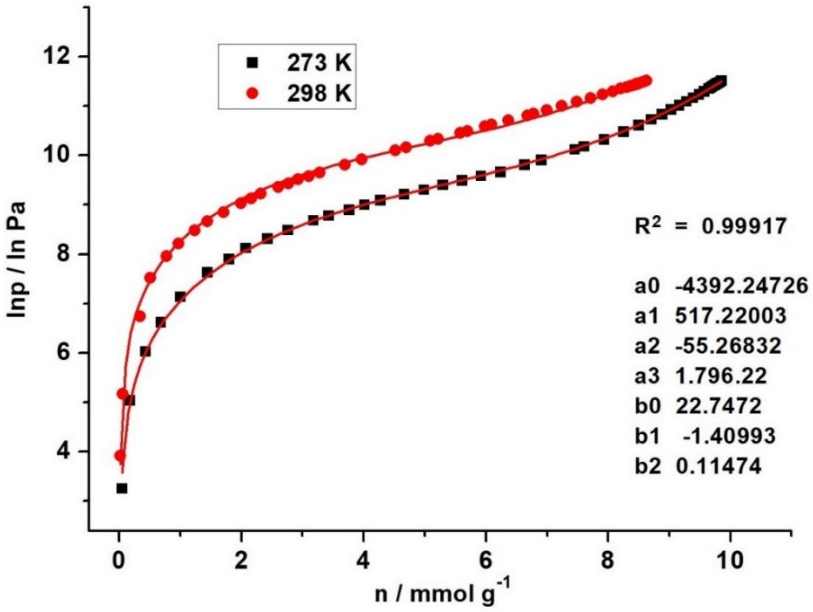
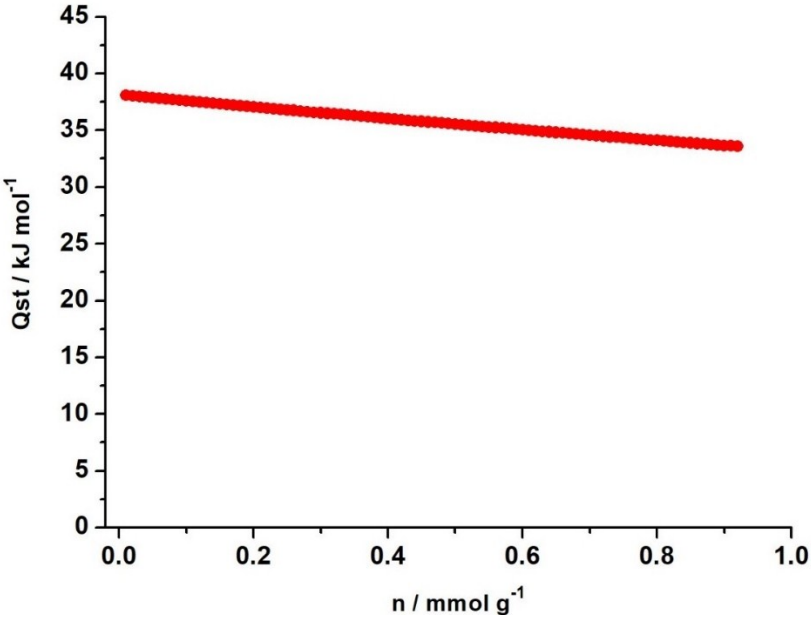


Fig. S5 The adsorption isotherms of CO_2, CH_4 and N_2 at 298 K along with the dual-site Langmuir Freundlich (DSLF) fits.



(a)



(b)

Fig. S6 (a) The calculated virial equation isotherms parameters fit to the experimental CO_2 data of **1a**. (b) The isosteric adsorption enthalpy for **1a**.

CO_2/N_2 and CO_2/CH_4 Selectivity Prediction by IAST Model

The experimental isotherm data for pure CO_2 was fitted using a dual Langmuir-Freundlich (L-F) model (equation (1)) and the experimental isotherm data for pure N_2 or CH_4 was fitted using Langmuir-Freundlich (L-F) model (equation (2)):

$$q = \frac{M_1 * K_1 * p}{1 + K_1 * p} + \frac{M_2 * K_2 * p}{1 + K_2 * p} \quad (1)$$

$$q = \frac{M * K * p}{1 + K * p} \quad (2)$$

Where q and p are adsorbed amounts and the pressure of component i, respectively. The adsorption selectivities for binary mixtures of CO_2/N_2 and CO_2/CH_4 were respectively calculated using the Ideal Adsorption Solution Theory (IAST), defined by

$$S_{i/j} = \frac{x_i * y_i}{x_j * y_j}$$

Where x_i is the mole fraction of component i in the adsorbed phase and y_i is the mole fraction of component i in the bulk.

Estimation of the isosteric heats of gas adsorption

A virial-type[S9] expression comprising the temperature-independent parameters a_i and b_i was employed to calculate the enthalpies of adsorption for CO_2 (at 273 and 298 K) on **1a**. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j$$

Here, P is the pressure expressed in Pa, N is the amount adsorbed in mmol g^{-1}, T is the temperature in K, a_i and b_j are virial coefficients, and m, n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial

coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^j$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

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